



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/NO86/00059 <b>(22) International Filing Date:</b> 20 August 1986 (20.08.86)  <b>(31) Priority Application Number:</b> 853303 <b>(32) Priority Date:</b> 22 August 1985 (22.08.85) <b>(33) Priority Country:</b> NO  <b>(71) Applicant (for all designated States except US):</b> NORSK HYDRO A.S. [NO/NO]; Bygdøy Allé 2, N-0257 Oslo 2 (NO).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> DAHL, Ivar, M. [NO/NO]; Kongsberggt. 6, N-0467 Oslo 4 (NO). FONNE, Gunnar [NO/NO]; Øvaldv. 23, N-3920 Eidanger (NO). THORSHAUG, Niels, Peter [NO/NO]; Høgenhei 15, N-3960 Stathelle (NO).		<b>(74) Agent:</b> ROSENBERGER, Bjørn; Norsk Hydro a.s., Bygdøy Allé 2, N-0257 Oslo 2 (NO).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PREFORM WITH GRADED REFRACTIVE INDEX AND METHOD FOR CONSTRUCTION OF THE SAME		
<b>(57) Abstract</b>  A preform with a graded refractive index of synthetic material, i.e. optically clean polymer compounds, constructed by means of a technique where monomers with additives are supplied to a rotating tube (1) with end pieces (2' and 2'') via a cannula (4) in a continuous or discontinuous flow and so that the monomer composition is changed from a lower refractive index toward a higher refractive index from the periphery of the preform toward its rotation axis. Monomered material which is deposited during the rotation of the tube (1) is caused to polymerize by means of radiation with UV beams and/or by means of radical polymerization.		

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Preform with graded refractive index and method for construction of the same.

The present invention concerns a preform with a graded refractive index and a method for the construction of preform materials for drawing or extruding optical fibres.

When electromagnetic waves are transmitted through a material, the transmission speed will depend on the refractive index of that material. If we apply electromagnetic waves with the same speed as visible light, we may, to make it simple, say that the electromagnetic wave is transmitted through the material with the speed of light. If we then imagine that the light is to be transmitted in a material with a larger refractive index than for instance air, then the speed of light will be slower in this material than in air. This is in accordance with Snell's law.

As a consequence of the above, one may say that light which is travelling along the axis of an optical fibre will be transmitted at a definite speed depending upon the refractive index of the fibre.

Light that does not follow the fibre axis but is transmitted outside the axis, will either be refracted from the outer limit of the fibre, i.e. the area between the fibre material and the cladding, or it may escape from the fibre.

This means that the light that travels through the fibre, will lose some intensity on its way from the place of origin to its destination. We say that the light is attenuated. Moreover, the refracted light will arrive with a certain phase displacement in relation to the light which follows the fibre axis because of the long distance the reflected light must travel.

For practical purposes one may say that the above phenomenon is present in the so-called stepped index fibres, i.e. fibres where the material has a uniform refractive index from the axis to the next alteration of the refractive index, which is usually between the inner core of the fibre and the cladding.

Information which is sent through such fibres in the form of light impulses will, in other words, be erased as the light impulses are transmitted through the fibre.

However, if we use optical fibres which are optically non-homogenous (graded index profile) i.e. the refractive index changes continually from a higher refractive index in the fibre axis to a lower refractive index peripheral fibre, the light which is transmitted through the fibre will not be refracted as in stepped index fibres, but will be continually bent toward the axis.

Information in the form of light impulses that are transmitted through such fibres, will arrive at its destination almost simultaneously, and the signals will therefore be easy to interpret.

This characteristic in graded index fibres has been known for some time and has been successfully applied when transmitting information in optical fibre of glass and quartz.

However, no description exists of optical synthetical fibres based on this principle. Thus the existing literature only describes homogenous fibres based on the principle of step index fibres.

U.S. patents 4.138.194 and 4.161.500 describe a method for the construction of preforms where the material is optically homogenous. A copolymer is used based on a methyl methacrylate and a small amount of additive consisting of other acrylates and methacrylates. The finished preform is in turn used for extruding optical fibres.

DE patent application No. 14 97 545 also describes construction of stepped index fibres where the fibre core is based on polystyrene, and where the fibre cladding is based on polymethyl methacrylate. The construction consists of filling the core material in a tube of polymethyl methacrylate, so as to produce a preform with a polystyrene core and a polymethyl methacrylate cladding. The preform is then heated until it becomes pliable, whereafter the optical fibre is extruded.

Optical fibres produced from preforms of the above-mentioned type, will be optically homogenous, and thus be less suited for transmission of information over long distances.

It has now surprisingly become apparent that it is also possible to make optical fibres from synthetics with a graded index where the refractive index is continually reduced from the fibre axis out toward the peripheral fibre. According to the invention, this is done by bringing together monomers with almost identical reaction parameters and solubility parameters, but with different refractive indices while continually changing the mole ratio of the monomers.

In accordance with the invention, the monomers are thereafter deposited on a rotating wall of glass, quartz and/or another suitable material, for instance a tube-shaped polymer material suitable for the cladding.

The monomers are then polymerized according to an accepted method, for instance by using initiators based on peroxide either by radiation, e.g. by applying UV radiation or by applying IR radiation for heating or a combination of one or two of the above-mentioned methods of polymerization.

If polymerization takes place in connection with the use of a glass cladding, and UV radiation is used in connection with the polymerization, then the UV radiation should have a frequency which coincides with the lowest UV absorption in the glass.

In order to get a better understanding of the invention, it is referred to Fig. 1 which shows a sideview of an apparatus for the construction of preforms.

The apparatus shown in Fig. 1 consists of an outer tube (1) of glass, quartz or plastics. Glass here means all qualities of glass. Plastics will include both water soluble and non-soluble materials, both natural and synthetic.

The tube (1) is plugged with the end pieces (2' and 2'') which have several functions. First of all the end pieces (2' and 2'') will act as a supporting member for the tube (1), and secondly function as pivoting point for the tube (1).

The device for the rotation of the tube (1) may be of a traditional kind, where the pieces (2' and 2'') are equipped with shaft ends, or rotation can take place directly over the end pieces when these are fastened to a rotating bearing. The device for the rotation of the tube is not part of the invention and is therefore not shown in Fig. 1.

The end pieces (2' and 2") are fastened to the tube (1) in a traditional way, for instance by screws, by tightening with O-rings of an inert material or by another form of friction coupling between the end pieces and the tube.

The end pieces may be made of metal and/or plastics. It would be an advantage if the material in the end pieces is resistant to corrosion by the monomers and that they are heat resistant, i.e. that they do not lose their shape through exposure to heat. The end pieces (2") are shown as a bushing (3) and as a cannula (4) which can be moved backwards and forwards in the tube (1) through the end piece (2"). Such movement is controlled by means of a motor (5), and is indicated by a double arrow over the cannula (4).

In order to prevent oxygen and dust particles from entering the tube (1) between the end pieces (2' and 2") one may for example feed nitrogen as inert gas (I) into the tube (1) along the bushing (3). The reagents, in this case consisting of the monomers  $M_1$  and/or  $M_2$  or of pure monomers or a mixture of them, are led through the cannula. It is not imperative to use only one or two monomers, as it is possible to visualize monomer combinations consisting of both two and more monomers. Therefore, the invention does not set a limit as to how many monomers are to be used or which will be utilized. The deciding factor for the choice of monomers is the optical characteristics and other physical data for the finished product.

The cannula (4) is coupled to the tube for feeding monomer ( $M_1$  and  $M_2$ ), UV-initiator, chain transfer and, if applicable, other auxiliary material (H) suitable for the purpose.

The apparatus described above has two movements. In the first place the tube (1) with the end pieces (2' and 2") will

rotate. Secondly, the cannula (4) will move backwards and forwards inside the tube (1) so that after a while the inner surface of the tube will be coated with material from the cannula (4).

The preform apparatus rotates at such a high speed that the materials will be evenly distributed. The minute the materials start to sink, the rotation speed is too low. Experience has shown that it is possible to choose rotation speeds between 500 and 2 000 rpm, preferably around 1 000 rpm.

As mentioned above, the cannula (4) will receive separate supplies of the monomers  $M_1$  and  $M_2$ , but it may also be an advantage to have a third supply, for instance chain transfer and/or UV initiator.

One may also use other initiating methods, such as use of peroxides and azo-compounds for the formation of free radicals for the initiation.

It is an advantage for subsequent usage that the preform constructed is as optically clean as possible, i.e. that it contains a minimum of materials that may distort the optical signals and attenuate them. It is therefore an advantage to initiate the polymerization and to carry this out by means of UV radiation.

It should be noted that it is difficult to dispose the polymerization heat in the preform if one uses systems which are initiated by means of for instance peroxides. It is therefore preferable to apply the simpler and cleaner polymerization method by means of UV radiation.

If UV radiation is used, the tube (1) must be permeable for this kind of radiation. In reality this means that one has to choose UV beams with a frequency between 300 and 400 nm.



Fig. 1 shows a device (7) for radiation with UV beams. Since the tube (1) rotates at a comparatively high speed, the radiation must be considered as being even over the entire inner surface of the tube (1).

It is not desirable to have a mole weight which is too high, since this will subsequently influence the speed of extrusion and the viscosity of the polymer. A chain transfer agent is therefore added in order to keep the mole weight in the correct mole weight area. Poly acrylates will have mole weights from 30 000 to 200 000, while polystyrene will be most suitable with mole weights between 100 000 and 500 000.

The purpose of the above-mentioned apparatus is to construct a preform with an attenuating refractive index from the rotation axis of the preform out toward the periphery.

This is achieved by supplying a monomer or monomers with the lowest refractive index to start with and the refractive index is thereafter increased with a continual alteration of the mole quantities of monomers  $M_1$  and  $M_2$ . At the end there will be a small cavity around the cannula (4) which is without polymers. When this cavity has reached the minimum size and before it joins the cannula, the cannula must be retracted and the cavity filled with the final monomer mixture, i.e. the monomer or the monomer mixture which has the highest refractive index. Then the preform is polymerized once again until polymerization is even.

The statement made above assumes that the refractive index profile in the stepped index fibre is attenuating evenly from the fibre axis out toward its outer limit, i.e. the limit toward the cladding.

We should also mention that according to the present method it should be possible to construct any type of optical fibre

according to the stepped index fibre principle if the refractive index profile is evenly or parabolically attenuating or diminishing in another way. It is also possible to produce stepped index fibres according to the method mentioned in that the polymer layers inside the tube (1) are built up by polymers, layer after layer, with an increasing refractive index from the tube (1) and toward the axis of the preform.

UV radiation of monomers may take place at all temperatures, but we choose a temperature which does not lead to temperature increases in the preform. Experience has shown that room temperature (approx. 20° C) or lower is very suitable if polymerization is carried out with UV radiation.

Below is an example of a typical combination of of the materials supplied for construction of the preform:

Monomer $M_1$	High refractive index	0 to 100 mole %
Monomer $M_2$	Low refractive index	100 to 0 mole %
UV-initiator		0.01 to 1 mole %
Chain transfer		0.01 to 1 mole %

As monomer  $M_1$  and  $M_2$  one would preferably choose the ones which have a reaction parameter = 1.0, i.e.  $r_1 = r_2 = 1.0$ , but reaction parameters may also be different from 1.0.

At the same time the solubility parameters  $\delta_1$  and  $\delta_2$  of monomers  $M_1$  and  $M_2$  ought not to have a larger difference than  $\Delta\delta = 1.0$ , but this is not of vital importance since there are monomer systems where the difference mentioned is larger but where the monomers nevertheless still are soluble.

Patent claims

1. Preform with a graded refractive index, characterized in that the preform consists of a system with polymer compounds with attenuating refractive index,  $n_D^{20}$ , from the rotary axis of the preform towards the periphery of the preform and where the polymers in the preform have been created by a continuous or discontinuous supply of monomers and/or monomer mixtures with increasing refractive index and the necessary additives and that said monomers are polymerized by means of radiation and/or by radical polymerization.
2. Preform according to claim 1, characterized in that ultraviolet radiation (UV radiation) is used for polymerization of monomers and that the wave length is from 200 to 400 nm, preferably from 300 to 400 nm.
3. Preform according to claims 1 and 2, characterized in that UV initiator is used, and/or chain transfer by polymerization.
4. Preform according to claim 1, characterized in that organic peroxides are used and/or azo-compounds by radical polymerization.
5. Process for the production of preform with graded refractive index according to claims 1-4, characterized in that there in a device consisting of an outer tube (1), which are finished with the end pieces (2' and 2")

and where the tube and the end pieces are caused to rotate around the linear axis, whereafter the monomerized material with the necessary additives is supplied to the tube (1) via a cannula moving backwards and forwards (4) in such a manner that the tube's (1) inner surface is covered by a layer of monomer which is brought to polymerization by means of radiation and/or by radical polymerization and that the further build-up of the monomer layers followed by polymerization of same takes place continuously or discontinuously so that the constructed preform is made up of polymers in connection with an increasing refractive index from the periphery of the preform toward the rotation axis of the preform and that the cannula (4) at the end is retracted out of the preform before the preform is completely filled with polymers and that the cavity which has been created in the preform is filled with a monomer of the highest refractive index which thereafter is polymerized.

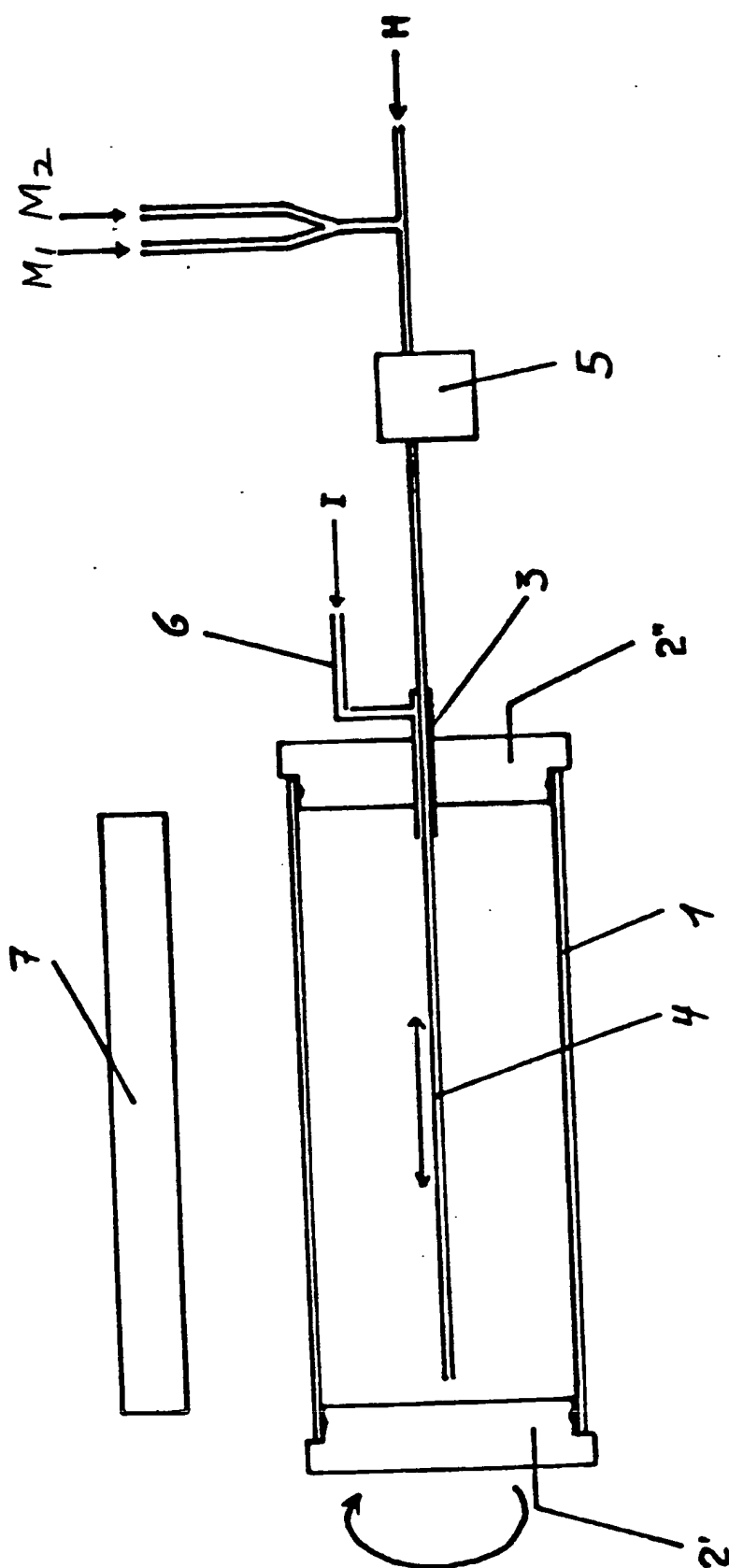



FIG. 1

# INTERNATIONAL SEARCH REPORT

International Application No **PCT/NO86/00059**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC 4		
B 29 D 11/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched 7		
Classification System	Classification Symbols	
IPC US C1	B 29 D 11/00 264: 1-2, 174, 240; 350: 96; 351: 169; 427: 163	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
SE, NO, DK, FI classes as above		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b>		
Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
X	US, A, 4 521 351 (OHTSUKA, YASUJI ET AL.) 4 June 1985 Totality & JP, 59137904 JP, 59137906	1-4
X	EP, A2, 0 144 712 (SUMITOMO CHEMICAL COMPANY LTD) 19 June 1985 Totality & JP, 60098407 JP, 60125807	1-4
X	US, A, 4 022 855 (HAMBLIN, DAVID P) 10 May 1977 Totality	1-4
A	EP, A2, 0 145 392 (EASTMAN KODAK COMPANY) 19 June 1985	1-5
A	US, A, 3 999 834 (OHTOMO, KOICHIRO ET AL.) 28 December 1976	1-5
.../...		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
1986-11-07	1986 -11- 13	
International Searching Authority	Signature of Authorized Officer	
Swedish Patent Office	 Claudia Oenhausen	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Patent Abstract of Japan, abstract of JP 60-119510 27 June 1985	1-5
A	Patent Abstract of Japan, abstract of JP 56-149004 18 November 1981	1-5
A	US, A, 3 955 015 (OHTSUKA, YASUJI ET AL.) 4 May 1976	5